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(72) Inventors KAKURO MURO, KUNIJI YASHIRO, HIDEAKI KANEKO and KIYOICHI YAMAZAKI

(19)

(54) SURFACE TREATMENT OF METALS

(71) We, PYRENE CHEMICAL SERVICES LIMITED, a British company, of Ridgeway, Iver, Buckinghamshire, SL0 9JJ, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for the treatment of metal surfaces and for the post-treatment of metal surfaces to which a chemical conversion coating has been applied, and by which the corrosion resistance of the surfaces is improved.

In conventional processes for treating metal surfaces in order to improve their corrosion resistance and the adhesion of paints which are subsequently applied, compositions comprising acids and salts of cations such as chromium, iron, manganese, aluminium, zinc and nickel, and anions such as phosphates, borates, nitrates, chromates and dichromates have been used to precipitate the insoluble salts onto the metal surface. However, the use of compositions containing ions such as chromium, zinc and manganese is restricted in view of the undesirable pollution which may be caused.

We have now found that a coating having improved corrosion resistance and good adhesion to paints can be formed on metal surfaces by a process which comprises applying to the surface a composition comprising an aqueous solution, dispersion or emulsion of a water-soluble titanium compound and from 0.1 to 12% by weight of a resin.

The coating formed by the process of this invention is found to have good corrosion resistance, possibly due to the presence of the titanium compound at the metal surface by virtue of its adsorption, the resin acting as a binder.

Metals which can be treated by this invention include iron, zinc and aluminium. The treated metal may first be treated with a conversion coating e.g. a conventional zinc-based phosphating or chromating composition.

The resins usable in this invention are preferably able to act as a binder, have high corrosion resistance, and high stability in the presence of water-soluble titanium compounds. Suitable resins include vinyl polymers and copolymers, e.g. vinyl acetate, vinylidene chloride or vinyl chloride polymers, acrylic polymers and copolymers, e.g. of acrylates, acrylic acid or methacrylic acid, polyurethanes, polyesters, polymers and copolymers of styrene and ethylene, aminoalkyl, alkyd and epoxy resins, natural and synthetic rubbers and natural high molecular weight resins.

The compositions used in the invention contain from 0.1 to 12%, and preferably from 2 to 12%, by weight of the resin. The precise figure depends on the type of resin used, its viscosity, and also the ultimate application.

Suitable water-soluble titanium compounds usable in this invention include K_2TiF_6, Na_2TiF_6, $(NH_4)_2TiF_6$, TiF_4, $Ti_2(SO_4)_2$ and $TiOSO_4$. The concentration of water-soluble titanium compound depends *inter alia* on its solubility and its stability in the presence of the resin. In general, the compound is present in the solution at from 0.1 to 10% e.g. 0.1 to 1%, by weight, but must be present in an amount sufficient to coat the metal e.g. above 0.05% by weight.

Novel compositions within this invention comprise aqueous solutions, dispersions or emulsions of from 0.1 to 1% by weight of a water-soluble titanium compound and from 0.1 to 12% by weight of a resin.

In order to improve the solubility of the titanium compound, to adjust the pH of solution or to stabilize the resin composition, amines such as ethylamine, dimethylamine, triethylamine and hexylamine, alkalis such as ammonia, caustic soda and caustic potash, and inorganic acids such as phosphoric acid, nitric acid, sulfuric acid and hydrofluoric acid may be employed.

In order to form the treatment compositions, the titanium compound may first be dissolved in water, and then the resin added to form the solution dispersion, or emulsion. Alternatively, the resin may be dissolved or dispersed into water to form the solution or emulsion

and then the water-soluble titanium compound added as the solid or in solution, or both the water-soluble titanium compound and the resin may be added together to form the composition. The proportion by weight of resin to water-soluble titanium compound is preferably from 100:1 to 1:10 and more preferably from 20:1 to 1:1.

The treatment composition, containing a pigment if desired, may be applied to the metal surface to be treated by immersing, pouring, brushing or spreading by means of a roller. The treated surface may then be allowed to stand or may be dried to form a tough coating having good corrosion resistance. The coating or immersion process is generally conducted at a temperature of from room temperature to 80°C. The drying operation is generally carried out at a temperature of from 80 to 250°C, for 0.2 to 10 minutes.

The coating formed by the process of this invention has excellent corrosion resistance and provides good adhesion to paints.

This invention will now be illustrated by the following examples, in which all percentages are by weight.

Example 1.

1 gm. of potassium titanium fluoride (K_2TiF_6) was dissolved in 500 ml of water and the solution was mixed with 50 gm of an aqueous 46% emulsion of an acrylic resin (Primal E—269 prepared by Nippon Acryl Co.) and made up to 1 litre by diluting the emulsion with water, to prepare a treating emulsion containing 2.3% of the acrylic resin and 0.1% of potassium titanium fluoride.

This treating emulsion was applied to a degreased and cleaned aluminium plate of 2S type by immersion and the coated aluminium plate was dried at 120°C for 3 minutes. The treated plate was then subjected to corrosion tests based on the saline spraying test according to JIS Z—2371. The results are shown in Table 1.

TABLE 1

Test Period	Aluminium plate coated with 300 to 350 mg/m² of	
	2.3% acrylic resin emulsion	Solution of Example 1
100 hrs.	60 to 80 development of white stain	Unchanged
200 hrs.	100% development of white stain	Unchanged

Example 2.

1, 3 and 5 gm, respectively, of ammonium titanium fluoride [$(NH_4)_2TiF_6$] were dissolved in 500 ml water and each solution was mixed with 50 gm. of an aqueous 40% emulsion of an acrylate resin (Tocryl N—142 prepared by Toyo Ink Co.) as a binder and made up to 1 litre of water. Each resulting emulsion was adjusted to a pH value of from 1 to 2 by adding 75% phosphoric acid (10 grams).

Degreased and cleaned aluminium plates of 2S-type were brushed separately with each treating emulsion and dried under the same conditions as in Example 1. The coated Al plates were subjected to the corrosion resistance test based on the same saline spraying test as in Example 1. Similar degreased and cleaned aluminium plates were coated with a conventional paint solution for protecting cans by means of a barcoater and dried at 180°C for 6 minutes to prepare coated specimens having a film thickness of 3μ. All specimens were then immersed in pure water at 80°C for 30 minutes and the whitening of the films were compared. The results are shown in Table 2.

TABLE 2

$(NH_4)_2TiF_6$ g/l	75% H_3PO_4 g/l	Saline spraying test		Whitening test
		168 hrs.	500 hrs.	
0	0	100% stained	–	100% whitened
0	10	100% stained	–	100% whitened
1	10	unchanged	50% stained	100% whitened
3	10	unchanged	unchanged	unchanged
5	10	unchanged	unchanged	unchanged

Example 3.

SPC—1 iron was degreased, cleaned and treated with a zinc based phosphating solution (Bonderite 137 prepared by Nippon Parkerizing Co.). The pretreated plate was then immersed in an aqueous emulsion containing ammonium titanium fluoride [$(NH_4)_2TiF_6$] at a concentration of 10 grams/litre and an acrylate resin emulsion (Tocryl X—2009 prepared by Toyo Ink Co.) at a solid resin concentration of 3%, and subsequently dried at 120°C for 3 minutes. The treated plate was subjected to the corrosion resistance test based on the same saline spraying test as in Example 1. The results are shown in Table 3.

TABLE 3

Post-treatment	Saline spraying test		
	0.5 hrs.	1 hr.	2 hrs.
None	100% red stained	–	–
Acrylate resin emulsion only	10 to 30% red stained	80% red stained	100% red stained
Emulsion of Example 3	unchanged	unchanged	unchanged

Example 4.

Galvanized steel plate was degreased, cleaned and pretreated with a zinc based phosphating solution. The pretreated film was then coated with an aqueous dispersion containing aluminium titanium fluoride at a concentration of 10 gm./l and polyvinylidene chloride (derived from Diophane 290D prepared by Petroleum Chemical Badisch Co.) at a solid resin content of 10% as a binder, by a roller coating process, and then dried at 120°C for 3 minutes. The post-treated plate was subjected to the corrosion resistance test based on the saline spraying test as in Example 1. The results are shown in Table 4.

TABLE 4

Post-treatment	1 hr.	2 hrs.	Swelling width after 120 hrs*
None	50% whitened	100% whitened rust observed	10 to 20 mm
Polyvinylidene resin emulsion only	3% whitened	80% whitened rust observed	10 mm
Emulsion of Example 4	unchanged	20% whitened rust observed	less than 3 mm

* Saline spraying test after coating with an aminoalkyd paint to a thickness of 20μ.

WHAT WE CLAIM IS:—

1. A process for forming a coating on a metal surface which comprises applying to the surface a composition comprising an aqueous solution, dispersion or emulsion of a water-soluble titanium compound and from 0.1 to 12% by weight of a resin.

2. A process according to claim 1 in which the resin is selected from polymers and co-polymers of vinyl compounds, acrylates, urethanes, esters, styrene and ethylene, amino-alkyl, alkyd and epoxy resins, natural and synthetic rubbers, and natural high molecular weight resins.

3. A process according to claim 1 or claim 2 in which the composition contains from 2 to 12% by weight of the resin.

4. A process according to any preceding claim in which the composition contains from 0.1 to 10% by weight of the titanium compound.

5. A process according to any preceding claim in which the weight ratio of resin to titanium compound is from 100:1 to 1:10.

6. A process according to claim 5 in which the ratio is from 20:1 to 1:1.

7. A process according to any preceding claim in which the metal surface has previously been coated with a conversion coating.

8. A process according to claim 1 substantially as herein described with reference to any of the Examples.

9. A metal surface when coated by a process according to any preceding claim.

10. A composition comprising an aqueous solution, dispersion or emulsion of from 0.1 to 1% by weight of a water-soluble titanium compound and from 0.1 to 12% by weight of a resin.

11. A composition according to claim 10 additionally comprising an amine, alkali or inorganic acid.

12. A composition according to claim 10 substantially as herein described with reference to any of the Examples.

For the Applicants:
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
53/64 Chancery Lane, London, WC2A 1HN.

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